

I. Introduction to Water Chemistry (1/2 week)
 General Properties of Water
 Composition of Different Waters
 Methods of Expressing Concentrations
 II. Chemical Equilibrium (1 week)
 Thermodynamic Basis of Chemical Equilibrium
 Enthalpy, Free Energy, and Equilibrium Constant
 Non-ideal Behavior of Ions and Molecules in Solution
 III. Chemical Kinetics (1 and 1/2 weeks)
 Reaction Mechanism
 Reaction Rate Laws
 Temperature Effect on Reaction Rates
 Catalysis
 Empirical Rate Laws
 IV. Acid-Base Chemistry (7 weeks)
 Equilibrium Calculations * General Approaches
 Mass Balance, Charge Balance, and Proton Condition
 Equilibrium Relationships
 Graphical Techniques for Equilibrium Calculations
 Effects of Temperature and Ionic Strength on Equilibria
 Mixtures of Acids and Base Calculations for pH
 Determination
 pH Buffers and Buffer Intensity
 Carbonate System and Its Equilibria
 Alkalinity and Acidity
 Theory of Acid-Base Titration

V. Precipitation and Dissolution (2 weeks)
 Precipitation and Dissolution Kinetics
 Equilibria of Dissolution
 Solubility Product Concept
 Temperature Effect on Solubility
 Common Ion Effect
 Complexation and Solubility
 Solubility of Salts
 Solubility Phase Diagrams and Their Applications
 Ferrous and Ferric Carbonates and Hydroxides
 Theoretical Aspects of Precipitation
 VI. Oxidation-Reduction Reactions (1 week)
 Redox Stoichiometry and Equilibria
 Free Energy and Potential Half Reactions
 Electrode Potential and the Nernst Equation
 Electron Activity Concept
 Equilibrium Calculations
 Graphical Representation of Redox Equilibria
 Applications of pe-pC and pe-pH Diagrams
 Theories of Corrosion
 Application of the Galvanic Cell Concept
 Corrosion Control
 Iron Chemistry and Acid Mine Drainage
 Biologically Important Redox Reactions

BASIC WATER CHEMISTRY

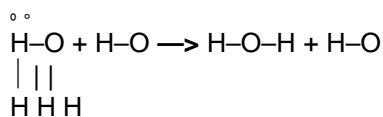
The Properties of Water

Water is the most common substance known to man, as well as the most important. In vapor, liquid or solid form, water covers more than seventy percent of the Earth's surface, and is a major component of the atmosphere. Water is also an essential requirement for all forms of life. Most living things are largely made up of water. Human beings, for example, consist of about two-thirds water.

Pure water is a clear, colorless, and odorless liquid that is made up of one oxygen and two hydrogen atoms. The chemical formula of the water molecule, H₂O, was defined in 1860 by the Italian scientist Stanislao Cannizzaro. Water is a very powerful substance that acts as a medium for many reactions, which is why it is often referred to as the "universal solvent." Although pure water is a poor conductor of electricity, impurities that occur naturally in water transform it into a relatively good conductor. Water has unusually high boiling (100° C/212° F) and freezing (0° C/32° F) points. It also shows unusual volume changes with temperature. As water cools, it contracts to a maximum density of 1 gram per cubic centimeter at 4° C (39° F). Further cooling actually causes it to expand, especially when it reaches the freezing point. The fact that water is denser in the liquid form than the solid form explains why an ice cube floats in a beverage, or why a body of water freezes from the top down. While the density property of water is of little importance to the beverage example, it has a tremendous impact on the survival of aquatic life inhabiting a body of water.

Ion Product Constant of Water

Water molecules are in continuous motion, even at lower temperatures. When two water molecules collide, a hydrogen ion is transferred from one molecule to the other (*Figure 1*). The water molecule that loses the hydrogen ion becomes a negatively charged hydroxide ion. The water molecule that gains the hydrogen ion becomes a positively charged hydronium ion. This process is commonly referred to as the *self ionization of water*.

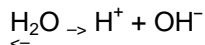


Hydronium Hydroxide

Ion Ion

FIGURE 1 Self Ionization of Water

The self-ionization of water does not occur to a great extent. This reaction can be written as a simple dissociation (*Figure 2*). At 25°C in pure water, each concentration of hydrogen ions and hydroxide ions is only 1×10^{-7} M. It is important to note that the amounts of hydrogen and hydroxide ions produced from this reaction are equal. This is why pure water is often described as a *neutral solution*.



Hydrogen Hydroxide Ion Ion

FIGURE 2 Dissociation of Water

In all other aqueous solutions, the relative concentrations of each of these ions are unequal. When more of one ion is added to the solution, the concentration of the other decreases. The following equation describes this relationship:

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ (mol/L)}^2 = K_w$$

The product of the hydrogen and hydroxide ions is always equal to $1 \times 10^{-14} \text{ (mol/L)}^{-14}$. Therefore, if the concentration of one ion increases by a factor of 10, then the concentration of the other ion must decrease by a factor of 10. Since this relationship is constant, it is given the symbol K_w , which is called the *ion-product for water*.

Aqueous solutions that have a hydrogen ion concentration greater than the hydroxide ion concentration are called *acidic solutions*. When the hydroxide ion concentration is greater than the hydrogen ion concentration, the solution is called *basic* or *alkaline*.

Molarity

The term "molarity" is used to describe the concentration of a substance within a solution. By definition, a one "molar" solution of hydrogen ion contains one "mole" of hydrogen ion per liter of solution. Therefore, a solution of 10 pH has 1×10^{-10} moles of hydrogen ions as shown by the following equation:

$$1 \times 10^{-10} \text{ mol} = \frac{1 \times 10^{-10} \text{g hydrogen ion}}{1 \text{L}}$$

Furthermore, a solution of 4 pH has 1×10^{-4} moles of hydrogen ions, and so on. This also means that one liter of a pH 10 solution would contain 1×10^{-10} grams of hydrogen ion, because 1 mole = 1 g/L for hydrogen.

A one molar solution of sodium hydroxide (NaOH), a base, is approximately 4% by weight, and has a pH value of 14. A one molar solution of hydrochloric acid (HCl), an acid, is approximately 3.7% by weight, and has a pH of 0. By diluting either of these two solutions, the molarity will decrease as well. For example, diluting 1 ml of HCl acid by adding 9 ml of distilled water results in a 0.1 molar hydrochloric acid solution which has a pH value of 1.0. Diluting sodium hydroxide using the same volumes yields a solution with a pH value of 13. If this dilution procedure was continued, the pH of each solution would approach a neutral pH of 7.

NOTE: For every 10-fold change in concentration (example: 0.1 to 1.0), the pH Changes by one unit.

If equal volumes of 4 pH (0.0001M HCl) and 10 pH (0.0001 NaOH) solutions were mixed together, the resultant solution would have a pH of 7.

NOTE: HCl and NaOH having opposing $[\text{H}^+]/[\text{OH}^-]$ concentrations.

The same result would apply when mixing equal volumes of a 6 pH acid and an 8 pH base, a 2 pH acid and a 12 pH base, and so on.